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[10191/1784]

METHOD AND DEVICE FOR PRODUCING SHAPED CERAMIC BODIES
 USING SETTER PLATES

[Background Information

] FIELD OF THE INVENTION

The present invention [is based on] relates to a method and a [corresponding] device for producing shaped ceramic bodies [according to the species defined in the generic claims.

Such a method is described, for example, in the German Patent 43 09 005 A1 in which a method was introduced].

10 BACKGROUND INFORMATION

In German Published Patent Application No. 43 09 005 is discussed a method for producing multilayer hybrids from a plurality of ceramic green sheets which contain organic auxiliary agents as binders and sintering aids, and which are provided with printed circuit traces and plated-through holes. The stack of green sheets is pressed together by two porous, ceramic setter plates during sintering and removal of the binder, to ensure the least possible shrinkage and buckling within the green sheets. To achieve a simple separation between the setter plates and the multilayer hybrid after the sintering process, the setter plates [were furthermore] are provided with a porous separating layer made, for example, of aluminum oxide which can be applied by slip casting or silk-screen printing. The organic auxiliary agents in the form of the binder or sintering additive are largely pyrolyzed

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during the binder removal or sintering, for example, in a hot press under axial pressure, and escape as organic bake-out products. In this context, the escape takes place, [inter alia]in part, via the porous setter plates or the applied porous separating layers which are gas-permeable. Damage to the ceramic sheets [due to]may result from burning out the organic auxiliary agents too quickly[,]. Damage may result from the diffusion of the broken-up, split-off or partially-burned organic bake-out products through the setter plates[, and the]. It is believed that there is a maximum portion of hydrocarbons in the oven atmosphere [in order](to remain below the explosion limiting values[are determinant of]) determine the speed for the duration of the binder removal and sintering process.

[The object of the present invention is to further develop the existing method in such a way that]SUMMARY OF THE INVENTION

An object of an exemplary method of the present invention is to provide a method in which the necessary period of time for the sintering and removal of binder from the shaped ceramic bodies is markedly shortened, without, for example, exceeding the explosion limiting values in the oven atmosphere.

[Advantages of the Invention

Compared to]It is believed that the [related art, the]exemplary method of the present invention[, having the characterizing features of the generic claims,] has the advantage that, by introducing a catalytically active substance into the pores of the porous setter plates and/or into the pores of the porous separating layers, a catalytic

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conversion of the gaseous bake-out products[, escaping] that
escape when baking out the green bodies[,] is at least
partially achieved. The bake-out products are, in
[particular]one exemplary embodiment, decomposition products
5 of the organic auxiliary agents and contain hydrocarbons,
among other things.

The escaping bake-out products are[preferably], in an
exemplary embodiment, converted into less combustible or
10 incombustible gases[, so that the]. In this manner, an
exemplary method of the present invention [makes it
possible]may be used to bake out more organic auxiliary agents
per unit of time than previously, without, for example, the
explosion limiting values for hydrocarbons being reached in
15 the oven atmosphere. [T] It is believed that this results in a
considerable time savings during the sintering and/or removal
of the binder from the green bodies, and thus to a shortening
of the oven cycles, which should mean[s] a marked cost
reduction and a substantially lower need for investment in
20 oven installations.

Moreover, it is believed that catalytically converted,
low-molecular oxidation or bake-out products diffuse more
quickly through the porous setter plates and the optionally
25 provided separating layers[,] than unconverted, high-molecular
bake-out products, which may mean[s] a further time savings
during production. [Incidentally, installations, existing
owing]According to [the]one exemplary method and/or device of
the present invention, installations for the catalytic
30 afterburning of the waste gases carried away from the ceramic
green bodies via the setter plates [can be designed to]may be

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smaller.

[I]According to one exemplary embodiment of the present invention, in addition to being introduced into the porous setter plates, the catalytically active substance [can]may also be introduced into the porous separating layers, which is believed to bring[s] with it advantages from the standpoint of process engineering. In [addition]an alternative exemplary embodiment, given an appropriate activity of the introduced, catalytically active substance, [in some cases]it [is]may even be sufficient if the substance is only in the porous separating layers, which should lead[s] to a markedly reduced need for these sometimes expensive materials. In the same way, for some purposes it [can]may be sufficient if the catalytically active substance is merely introduced into the surface area of the porous setter plates or separating layers, for example, by spraying on or impregnating. This may also reduce[s] material costs.

[More advantages and advantageous further developments of the present invention are apparent from the measures indicated in the subclaims.

Thus, one particularly advantageous refinement of the]Thus, in one exemplary method according to the present invention[uses], starting materials may be used which,[at the latest] in the course of a thermal after-treatment of the setter plates [and]and/or the separating layers, respectively, are converted to form metallic, nano-scale particles[and are located] in the pores of the setter plates and/or the separating layers.

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[Also very advantageous is] Another exemplary embodiment involves the selection of a metallic-salt solution as the starting material for introducing the catalytically active substance[, i]. In [the case of which] this exemplary
5 embodiment there may be no unwanted, in particular inorganic, residues [remain] remaining in the setter plates [or] and/or separating layers after the thermal after-treatment.

For faster removal of gaseous bake-out and conversion
10 products, it is believed that the setter plates [can advantageously] may be provided with additional gas outlets arranged, in particular, parallel to the surface of the setter plates.

15 [Drawing

] BRIEF DESCRIPTION OF THE DRAWING

The [single] Figure shows[a diagrammatic sketch of] a ceramic multilayer hybrid composed of a stack of ceramic sheets between two porous setter plates which are separated from the
20 stack of sheets by porous separating layers.

[Exemplary Embodiments

Exemplary embodiments of the present invention are explained
25 more precisely in the following with reference to the Figure.

] DETAILED DESCRIPTION

A shaped ceramic body, which, for example, can be one ceramic sheet, a stack of ceramic sheets or a ceramic multilayer hybrid
10 composed of ceramic sheets 1, 2, 3, 4, 5, [that] and
30 which is provided with printed circuit traces, switching elements and plated-through holes (not shown in the Figure),

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is situated between two porous setter plates 20, 21[which].
The two porous setter plates 20, 21 may, on the surface on the
side facing multilayer hybrid 10, [are]be provided with porous
separating layers 30, 31. Setter plates 20, 21 [are]may be
5 provided with gas outlets 22, e.g. in the form of channels
running parallel to the surface of the plates, for more rapid
removal of escaping gases. The shaped ceramic body[,] (that
is[to say], multilayer hybrid 10[,]) may exist[s] initially
as a green body and, in addition to ceramic components, may
10 also contain[s] organic auxiliary agents, e.g. in the form of
binders, sintering additives, softeners and residues of
solvents.

Setter plates 20, 21 [are]may be made of porous, ceramic
15 materials and [are]may be gas-permeable for organic bake-out
products which develop during binder removal and/or sintering
of the shaped ceramic bodies. They [are]may be preferably
gas-permeable for low-molecular, gaseous oxidation products
such as CO, CO₂, H₂O, CH₄, as well as simple hydrocarbons.

20 The process of sintering and/or removing binder from
multilayer hybrid 10 is carried out in a hot press under axial
pressure, setter plates 20, 21 in particular [preventing]may
prevent sintering shrinkage of multilayer hybrid 10 from
25 occurring in the plane of setter plates 20, 21. Since, because
of their fragility, it is very difficult to handle multilayer
hybrids 10 from which the binder has been removed, the entire
binder removal and sintering process must be carried out in
the hot press, although [typically]"typically" less than one
30 hour of 11.5 hr. of firing time is necessary for the actual
sintering under pressure. Essentially, the removal of binder

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from multilayer hybrid 10 by gradual bake-out is carried out during the remaining time, as a result of which the organic auxiliary agents are thermally decomposed to a great extent, or volatilize, undecomposed, from the green body and are carried away to the outside through the gas-permeable setter plates. Thus, essentially, the time for the diffusion of the cracked or partially-burned, organic constituents through setter plates 20, 21 is speed-determinate for the binder removal process. Since the organic constituents contain a high portion of hydrocarbon compounds, for reasons of operational safety (protection against explosion), the binder removal process must be carried out [in such a way]so that the concentration of hydrocarbons in the oven atmosphere always remains below the explosion limiting values.

Porous separating layers 30, 31 simplify the removal of ready-sintered multilayer hybrid 10 from setter plates 20, 21. For example, the separating layers contain essentially ceramic constituents such as aluminum oxide and are preferably applied on setter plates 20, 21 by silk-screen printing or slip casting. [However, t] The exemplary method of the present invention, however, can also be implemented without separating layers 30, 31. Porous separating layers 30, 31, like setter plates 20, 21, are gas-permeable for organic bake-out products from the ceramic green body.

[T]One aspect of the [essence]exemplary method and/or device of the present invention is the introduction of a catalytically active substance into setter plates 20, 21 and/or separating layers 30, 31 prior to beginning the actual process of sintering and/or removal of binder from the shaped

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ceramic bodies, in order to accelerate the implementation of this binder removal process.

Catalytically active noble metals such as palladium, rhodium or platinum are believed to be suitable for this purpose. The specific selection of the catalytically active substance in the individual case is made according to the type of the organic auxiliary agents and their quantity, as well as the sintering or binder-removal temperatures utilized, it always being important and/or necessary to take into account the catalytic activity of the respective material and its costs. The catalytically active substance is used specifically to catalytically convert organic auxiliary agents escaping from the green body during sintering and/or binder removal. To that end, it is believed to be very advantageous if it is located in the pores of the porous materials of setter plates 20, 21 and/or of porous separating layers 30, 31, where it is easily available for the escaping gases and can develop a suitably high activity. The catalytically active substance catalytically converts the organic hydrocarbon compounds contained in the escaping bake-out products by, for example, oxidizing them or converting high-molecular, organic hydrocarbon compounds to form low-molecular hydrocarbon compounds. In particular, it is used for the oxidation of easily combustible hydrocarbons into incombustible or non-explosive compounds which are then removed via the pores in setter plates 20, 21 and/or separating layers 30, 31, as well as via gas outlets 22.

The catalytically active substance can be introduced into setter plates 20, 21 and separating layers 30, 31,

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respectively, by dipping setter plates 20, 21 into an appropriate metallic-salt solution, or by spraying the surface area of setter plates 20, 21 with this solution. In this context, setter plates 20, 21 can already have been provided
5 with separating layers 30, 31 beforehand, so that the catalytically active substance is also introduced into separating layers 30, 31.

By dipping, the catalytically active substance is distributed
10 essentially uniformly within setter plates 20, 21, and optionally within separating layers 30, 31, as well. By spraying in particular the side of the porous plates facing the ceramic green body, the catalytically active substance is present largely on the surface on setter plates 20, 21 and
15 separating layers 30, 31, respectively. [One skilled in the art must check in the individual case, on the basis of a few simple experiments, which method is the most suitable in each case.] Spraying has the advantage that the quantity of catalytically active material used up is relatively small,
20 which means lower material costs. On the other hand, because of the distribution on the surface, only a small part of the volume of setter plates 20, 21 is catalytically active, which means a correspondingly longer or [more incomplete]less complete catalytic conversion of the organic bake-out
25 products. [However, since the catalytically active materials that are possible also differ with respect to their catalytic activity, one skilled in the art, through preliminary experiments, must find in the individual case an optimum between the material costs and the local distribution of the
30 catalytically active substance, as well as the degree of the catalytic conversion and the time resulting for the binder

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removal.]

In further exemplary embodiments, the catalytically active substance is introduced only into separating layers 30, 31, for example, by subsequent spraying[, it]. In this case again[being], it would be important and/or necessary in the individual case to weigh advantages and disadvantages from the standpoint of process engineering against material costs and the time savings attained during the binder removal.

To ensure a homogenous and very fine distribution of the catalytically active substance in setter plates 20, 21 and separating layers 30, 31, respectively, or in the corresponding surfaces, they are [preferably]in an exemplary embodiment steeped in an aqueous metallic-salt solution containing at least one of the metallic salts PtCl_6 , PdCl_2 , RhCl_3 , platinum acetate, rhodium acetate or palladium acetate. The concentration of the catalytically active substance in this metallic-salt solution [is preferably]may be between 0.1 g/l to 30 g/l. Concentrations of 1 g/l to 15 g/l have turned out to be particularly advantageous. In this case, in a setter plate 20 weighing 1 kg, when using a platinum solution containing 10 g of platinum to 1 liter of solution, approximately 0.6 g of platinum is introduced into setter plate 20. When using a solution containing[] 6 g of palladium to 1 liter of solution, approximately 0.4 g of palladium is introduced per plate.

After setter plates 20, 21 have been sprayed or dipped, a thermal after-treatment of setter plates 20, 21 with the introduced catalytically active substance is expediently

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carried out. Depending on the size of the plates, the type of metal introduced and the metallic-salt solution employed, this after-treatment lasts from 30 minutes to 5 hours at a temperature of 100° C to 700° C. [It is preferably] This may be
5 carried out in a gas atmosphere, such as air or nitrogen, which does not oxidize the catalytically active substance. However, when working with a few catalytically active materials which can be oxidized relatively easily, in order to avoid oxidation, it is believed to be best if work is carried
10 out in a reductive gas atmosphere. For example, in the case of platinum, rhodium and palladium, it is sufficient if the thermal after-treatment is carried out at 500° C over 2 hr. in air.

15 The use of organic metallic compounds, such as the acetates indicated, is particularly recommendable for applications in which no residues of the introduced metallic-salt solution are to remain in setter plates 20, 21 and separating layers 30, 31 after the thermal after-treatment, since these compounds
20 thermally decompose in a substantially residue-free manner during the thermal after-treatment.

[It has turned out to be particularly advantageous if] In another exemplary embodiment, the catalytically active
25 substance is present in the form of uniformly distributed, nano-scale, metallic colloids of, for example, platinum, rhodium or palladium in the pores of the porous setter plates and separating layers, respectively. [T] It is believed that the size of these colloids is advantageously between 3 nm and
30 100 nm, in order to attain the highest possible specific surface areas, and thus an effective seeding of setter plates 20, 21 or of separating layers 30, 31.

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[Abstract]

ABSTRACT OF THE DISCLOSURE

A method and [a] device for producing shaped ceramic bodies,
5 particularly ceramic sheets or multilayer hybrids[(10)]
provided with printed circuit traces, switching elements
and/or plated-through holes. The shaped ceramic bodies are
initially present as green bodies and also contain organic
auxiliary agents, [e.g.]for example as a binder. During
10 sintering and/or removal of the binder from the shaped ceramic
bodies, they are compressed between porous setter plates[(20,
21)] in whose pores a catalytically active substance is
introduced, so that the gaseous, organic, bake-out products of
the green bodies, these products developing during sintering
15 and/or binder removal, are catalytically converted when
escaping through the porous setter plates. The setter plates
[can furthermore]be provided with separating layers
[which]that likewise [can]may contain the catalytically active
substance. The [proposed]method should provide [leads to]a
20 considerable time savings when sintering and/or removing
binder from the shaped ceramic bodies.

25 [Figure]

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